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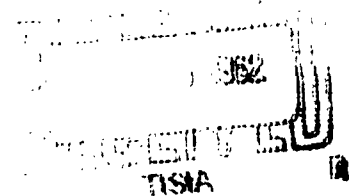6 2 - 3 - 1

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VAPORIZATION OF THE

Ti-B SYSTEM

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Mass Spectrometric Study of the Vaporization of the Ti-B System

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MASS SPECTROMETRIC STUDY OF THE VAPORIZATION
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I. ABSTRACT

A mass spectrometer has been used with Knudsen cells to study the vaporization of the titanium-boron system. The pressures of Ti(g) and B(g) have been determined over several condensed phases and yield ΔH^O_{298} = 430 kcal/mole and ΔH^O_{298} = -52 kcal/mole for the heats of vaporization and formation of TiB_2, respectively. Thermodynamic functions for TiB(s) have been obtained.

II. INTRODUCTION

Brewer and Haraldsen[1] have summarized thermodynamic information on some refractory borides and have made qualitative estimates of heats of formation based on the relative stabilities of boron-containing compounds at high temperatures. They mention the experimental difficulties associated with borides and suggest vapor pressure measurements as a promising approach to the evaluation of thermodynamic quantities. Vapor pressure measurements on elemental boron

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have been made by Chupka[2], Thorn[2], Schissel and Williams[3], and Akishin
et al[4], who find values in agreement for the heat of sublimation near
ΔH_0^O = 130 kcal/mole.

The qualitative observations of Brewer and Haraldsen[1] indicate a heat
of formation for $TiB_2(s)$ near -72 kcal/mole; this value is confirmed by
Samsonov.[5] However, mass spectrometric determinations of partial vapor
pressures by Schissel and Williams[3] showed TiB_2 to be more volatile than
would correspond to ΔH_f^O = -72 kcal/mole, leading to a value of about -32 kcal/
mole instead; the congruent vaporization of the Ti-B system as used by Searcy
et al[6] provided bounds for the relative electron impact ionization cross sections
for titanium and boron vapor and substantiated the conclusions of Schissel and
Williams; and a high temperature calorimetric measurement by Lowell and
Williams[7] resulted in ΔH_f = -50±5 kcal/mole.

A mass spectrometer was employed in the present work with Knudsen
effusion cells where the pressures of titanium and boron vapor were determined
from rates of effusion. The vaporization of TiB_2 was studied under several ex-
perimental conditions: (1) TiB_2 with excess boron added, (2) TiB_2, and (3) TiB_2
with excess titanium added. The results of each set of measurements were used
to compute the heat of vaporization of TiB_2, and current thermodynamic data
were used to obtain the heat of formation at 298°K.

III. APPARATUS

The mass spectrometer, similar to that developed by Inghram and co-
workers[8], was a 60° sector instrument of 12 inch radius, differentially pumped

by two 5-liter/sec ion-getter vacuum pumps.[*] Electron bombardment was used
to heat the Knudsen cells in an arrangement similar to that of Chupka and
Inghram.[9] A movable shutter interposed between the cell and the electron-impact
ionization source was used to distinguish neutral species from background non-
condensable molecules of the same mass. The energy of the ionizing electrons was
continuously adjustable from 5 to 150 ev for appearance potential measurements.
The main detector[**] was a twenty-stage electron multiplier employing Be-Cu
dynodes. Provision was also made to collect the ion beam directly on an adjustable
plate which could be moved in and out of the line of the ion beam. The output from
each collector was measured with an electrometer and recorded continuously on a
strip-chart recorder.

Temperature measurements were made with a Leeds and Northrup dis-
appearing-filament optical pyrometer sighted into small holes (0.030"dia, 0.060"
deep) in the sides of the Knudsen cells. The pyrometer was calibrated against a
standard lamp certified by the National Bureau of Standards to be accurate to $\pm 7\,^\circ$C
at the highest temperatures employed in this study. An auxiliary check was made
against a pyrometer calibrated by the National Bureau of Standards and no systema-
tic differences were noted. The calibration error was therefore taken to be $\pm 7\,^\circ$C.
The temperature correction for the sight window was determined before and after
all data were taken. The estimated total error was $\pm 20\,^\circ$ for the work with boron
added to TiB_2 and $\pm 10\,^\circ$C for the remaining measurements. Because of the high
emissivity of graphite and since the temperatures were measured by sighting in
holes in the graphite, no emissivity corrections were necessary. Further tests on

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the temperature measurements showed the above statement to be correct and further that temperature gradients in the cell were small. In an auxiliary vacuum system two pyrometers were simultaneously sighted on a tungsten ribbon filament to obtain their relative calibration. The Knudsen cell was then placed at the same position as the tungsten ribbon with one pyrometer sighted into the temperature measuring hole in the side of the cell and the second pyrometer sighted into the Knudsen effusion hole. At the temperatures used in the experiments for which Third Law calculations were made in this study no systematic difference could be measured, but at the very lowest temperatures, (1700°K), attained only during measurements pertaining to the Second Law treatment of the vaporization of boron, a temperature difference was noted but never exceeded 14°C.

IV. PROCEDURE AND RESULTS

The phase diagram shown by Brewer and Haraldsen[1] for the Ti-B-C system indicates the expected mutual stabilities of the various phases. This diagram was used to determine suitable crucible materials for the systems which were studied. For the experimental situations discussed below the phase systems are identified by the sample materials initially loaded in the crucible. Subsequent X-ray analyses of the samples after heating showed partial conversion to other phases, particularly in the boron and titanium rich cases. The experimental results are discussed in the light of the X-ray observations made at room temperatures after the runs. In this paper all solid-solid reactions are considered in the approximation $\Delta C_p = 0$ and therefore phases stable over limited temperature ranges are ignored.

<u>$TiB_2(s) + B(s)$</u> — X-ray analysis of an aliquot part of the TiB_2 and boron pow-
dered samples showed no detectable impurities, and spectroscopic analysis
showed 0.1% iron, 0.1% silicon and smaller amounts of chromium and other
metals. The samples were run in a B_4C crucible (11/32" diameter, 11/16"
long, 1/32" wall thickness) which was contained in a graphite outer jacket (15/16"
diameter, 1-1/4" long, 1/8" wall thickness). Two B_4C crucibles were made by
heating graphite crucibles in the presence of boron. The first crucible was used
to demonstrate the complete boronization of the graphite; the second was used for
the experimental runs. Both crucible and jacket had rectangular orifices 4.5 mm
long and 0.75 mm wide which provided a ratio of orifice area to sample area of
$\sigma_A \cong 0.04$ (sample area means gross exposed powder area, not the microscopic
area which may make the effective σ_A smaller).

After the sample was loaded, the Knudsen cell was heated slowly to the
temperature at which a shutter effect was observed on Ti^{48} and B^{11}. (These
isotopic signals were used for all the measurements, whereas signals at other
isotopic positions were used only to confirm the identification of the species).
During the preliminary outgassing period, gaseous titanium oxide and boron
oxide species were observed but disappeared completely after several hours of
heating. No data were taken until signals obviously characteristic of the oxide
species had disappeared and appearance-potential measurements indicated that
the B and Ti signals resulted solely from the elemental gases.

Data were taken on the temperature dependence of the boron signal and
were plotted according to the Clausius-Clapeyron relation to obtain the heat of

sublimation of boron, ΔH_T^o. Four experimental runs of this type were made.
The results for ΔH_T^o in kcal/mole obtained chronologically are: 130.2 ± 4.4 at
$1962\,^{\circ}K$, $128.4+1.2$ at $2085\,^{\circ}K$, 133.0 ± 2.2 at $2072\,^{\circ}K$, and 132.6 ± 1.5 at $2121\,^{\circ}K$,
where the errors are the statistical errors determined from least square analyses,
and the temperatures are the average midrange temperatures of the individual runs.
Figure 1 shows a plot of the data of the second run where the relative boron vapor
pressure $(I_B T)$ is plotted as ordinate against $1/T$ as abscissa. Tabulated data[2]
were used to reduce the ΔH_T^o values to ΔH_o^o with the results $\Delta H_o^o = 130.8\pm5.1$,
129.3 ± 2.7, 133.8 ± 3.4, and 133.5 ± 2.9 kcal/mole. The final error assignments
were obtained from the statistical combination of random errors from the least
square analyses and from the instrumental uncertainty in the absolute tempera-
ture (fractional error in $\Delta H_T^o = 2\,\dfrac{\Delta T}{T}$) as described by Trulson, et al[10]. A
powder pattern X-ray analysis of the sample after the runs showed strong TiB_2
lines and no boron lines. While the boron lines were weak even at the start, it is
possible that all free boron was lost during the courre of heating. Nevertheless,
the average of the above Second Law values, 131.9 kcal/mole, is only slightly
higher than mass spectrometric determinations using the Third Law[2,3,4] and
is in excellent agreement with recently tabulated data[2]. Therefore, computations
in this section will utilize the tabulated data for the vapor pressure of boron.

The titanium pressure was determined relative to the boron pressure
from

$$P_{Ti} = P_B\,\frac{I_{Ti}\,T\,Ti}{I_B T_B}\,\frac{(\sigma iS)_B}{(\sigma iS)_{Ti}} \qquad (1)$$

where P denotes the partial pressure, I the relative collected ion current, σ the cross section for ionization of neutral species, T the temperature, i the isotopic abundance correction factor, and S the electron multiplier conversion factor. The ionization cross sections computed by Otvos and Stevenson[11] were used, and the multiplier conversion efficiencies were determined directly for both boron and titanium signals. The relative ion signals were measured at the same temperature. Electron bombardment energies ranging from 15 to 60 ev were used, but were always normalized to 40 ev by means of appearance-potential data of relative signal intensity vs electron energy taken when the signals were large.

The boron and titanium pressures were used to obtain the equilibrium constant K for the reaction $TiB_2(s) \rightarrow Ti(g) + 2B(g)$. The free energy change was computed ($\Delta F_T^O = -RT \ln K$), and the heat of vaporization was obtained from

$$\Delta H_{298}^O = \Delta F_T^O + T \left(- \frac{\Delta F_T^O - \Delta H_{298}^O}{T} \right)_{Ti(s) \rightarrow Ti(g)} + 2T\left(- \frac{\Delta F_T^O - \Delta H_{298}^O}{T} \right)_{B(s) \rightarrow B(g)} \tag{2}$$

where tabulated[2] free energy functions for Ti and B were used, and free energy functions for $TiB_2(s)$ were assumed equal to those for $Ti(s) + 2B(s)$. This assumption has been shown to be valid up to 700 °C by Walker, et al[12]. The heat of formation of $TiB_2(s)$ was computed from ΔH_{298}^O and the tabulated[2] heats of sublimation of boron and titanium.

Data used to compute the heat of vaporization of TiB_2 are given in Section 1 of Table I. Ten determinations of P_{Ti} relative to P_B were made over a

temperature range of approximately 200°K. The table gives the equilibrium

constant, free energy change, and heat of vaporization of $TiB_2(s)$. The average

heat of vaporization at 298°K is 431.4±5.9 kcal/mole, and the heat of formation

is -53.7±5.9 kcal/mole.

TiB_2 in graphite — A crucible fabricated from "National" TSX graphite was

used with a TiB_2 powdered sample. The knife-edged circular orifice in the

crucible lid was 0.75 mm in diameter to give $\sigma_A \leq 5 \times 10^{-3}$. In a preliminary run

the crucible was heated empty to the highest temperatures anticipated for the

TiB_2 measurements to demonstrate that no boron background impurity signals

were present. The TiB_2 sample was then loaded with a 5 mg silver calibration

charge and heated to approximately 1100°C where the silver charge was allowed

to vaporize completely. This method of calibration has been described by Chupka

and Inghram[9]. The pressures of titanium and boron were determined from ion

intensity data taken at higher temperatures according to the relation

$$P_x = \frac{I_x T}{K_{Ag}} \frac{(\sigma iS)_{Ag}}{(\sigma iS)_x} \qquad (3)$$

where I_x denotes the relative ion current for species x (titanium or boron), T

the cell temperature and (σiS) as described in Equation 1. The constant K_{Ag}

represents the effective sensitivity constant (the collected charge per effused

neutral particle) for the mass spectrometer determined from the silver calibra-

tion measurements.

The relative intensities of the boron and titanium signals were observed to increase slowly with time at fixed crucible temperature. Since boron already had the higher partial pressure, this further increase would be paradoxical if titanium and boron only were present. However, equilibration with carbon, while having little effect on the integral free energy for the reaction $TiB_2(s) \rightarrow Ti(g) + 2B(g)$, can change the partial molal free energies of the titanium and boron markedly. In other terms, the equilibrium constant should remain nearly unchanged when carbon is added while the partial pressures may change significantly.

Equilibrium constants and integral free energies of evaporation were calculated by the Third Law method outlined in equation 2. Ten determinations of P_{Ti} and P_B were made over TiB_2 in graphite and are given in Table I Section 2. These results yield $\Delta H^O_{298} = 429.6 \pm 5.4$ kcal/mole for the vaporization of TiB_2 and $\Delta H^O_{298} = -51.9 \pm 5.4$ kcal/mole for the heat of formation.

$Ti+TiB_2$ — Excess titanium was added to the graphite crucible containing the TiB_2 sample used in the runs described above. The crucible was heated for several hours above the melting point of titanium to allow complete reaction, and subsequent X-ray analysis of the sample showed TiB_2 only, while the inside of the crucible lid showed C and TiC. Additional titanium was added and the heating process was repeated; again the reaction occurred but at much slower rate. A third loading of titanium was added with a weighed amount of silver. A silver calibration was performed at 1100°C and was in agreement ($\sim 10\%$) with other calibrations. The vapor pressure of solid titanium was determined from Equation 3: at 1842°K, $P_{Ti} = 1.0 \times 10^{-6}$ atm; at 1858°K, $P_{Ti} = 1.6 \times 10^{-6}$ atm; and at 1722°K, $P_{Ti} = 1.1 \times 10^{-7}$ atm. These results are in excellent agreement with tabulated data[2] and are used to confirm the ionization cross sections computed by Otvos and

Stevenson[11] for titanium. While Ti(s) cannot be in equilibrium with C, TiC and TiB$_2$, it is assumed the reaction rate was sufficiently slow after the crucible had been previously exposed to titanium at much higher temperatures to sustain the pressure over solid titanium though the pressure of pure titanium was not sustained over the more reactive liquid. This assumption is corroborated by the observation that even after the second loading of titanium, a plot of ln P_{Ti} vs $\frac{1}{T}$ taken before the titanium was melted yielded a heat of sublimation of titanium only seven kilocalories larger than given in the JANAF tables.

Below the melting point of titanium the boron signal could not be observed, but at higher temperatures both signals were measured. At the higher temperatures the reaction of titanium again became evident since the vapor pressure (which was determined after each of the three successive titanium loadings) of liquid titanium could not be maintained, although the pressure exceeded that to be expected over TiC + C.

The pressure data are given in Section 3 of Table I and unlike the previous results were not obtained at a fixed position in the phase diagram. As excess titanium was added different phases formed and X-ray analyses showed TiC + C + TiB$_2$ after the first heating and TiC + TiB (orthorhombic) + TiB$_2$ after the final heating. The effect of the additional titanium manifests itself in a 20-fold increase in titanium pressure at 2300°K as inspection of the values of P_{Ti} in Section 3 of Table I will show and corresponds to the formation of TiB. Titanium diboride was always present and each set of pressures gives consistent values for its heat of vaporization. Results for eleven sets of data give an average heat of vaporization for TiB$_2$ of 428.6±5.3 kcal/mole and a heat of formation of -50.9±5.3 kcal/mole. The pressures from run No. 10 of Table I taken in the TiC-TiB-TiB$_2$ region of the phase diagram yield

for the reaction $TiB(s) \rightarrow Ti(g)+B(g)$, $\log K_{2340} = -11.07$, $\Delta F°_{2340} = 118.5$ kcal/mole, and $\Delta H°_{298} = 279$ kcal/mole. The associated heat of formation of TiB(s) at 298°K is -34 kcal/mole.

Summary — Data from all the experimental points given in Table I are shown in Figure 2. The equilibrium constant for vaporization of TiB_2 is given as a function of reciprocal temperature. The least-square line through the data gives a heat of vaporization $\Delta H°_{2287} = 424\pm14$ kcal/mole and $\Delta H°_{298} = 435$ kcal/mole in excellent internal agreement with the Third Law computations.

Searches for Ti-B gaseous species were negative; for example, at 2426°K, $P_{TiB(g)}$ was less than 10^{-9}atm during the $B+TiB_2$ runs. Similar bounds for other simple combinations occurred and, in general, extended sweeps through mass 600 indicated no species to ~ 1% of the B(g) signal. A search for $B_2(g)$ was negative and indicated P_{B_2} was less than 4×10^{-9}atm at 2316°K over $B + TiB_2$. This bound is not low enough to test the tabulated data.[2]

Some impurity signals were observed. In addition to the oxide species which volatilized, elemental Fe(g) and Cr(g) impurities were observed and never completely disappeared. During the final runs where excess titanium was added the pressure of Cr(g) was comparable to Ti(g) even though spectroscopic analysis showed the Ti(s) to contain no Cr. It is presumed that chromium borides in the TiB_2 at trace levels were converted to titanium borides and excess chromium. The rather high impurity level of Cr on the inside of the lid corroborates this assumption.

Some unexplained signals occurred at the mass 30 through 36 positions which appeared by every test to be legitimate neutral species leaving the cell during the work with $B+TiB_2$ in B_4C. It is believed they are not related to the Ti-B system but are possibly gaseous B-C species.

In all the previous results the net experimental error assignment comprised the random uncertainties obtained as the standard deviation of the mean compounded with the instrumental uncertainties obtained from the estimated errors in the temperature and vapor pressures. The temperature error has been discussed above; the pressure error was determined from uncertainties in the relative ionization cross sections and in the measured relative multiplier gains for the several species. The internal agreement between the Second and Third Law measurements by Chupka[2] and of the Third Law measurements by Schissel and Williams[3] and of the Second Law data herein presented on the sublimation of boron shows that the relative cross sections σ_B / σ_{Ag} predicted by Otvos and Stevenson[11] are in error by less than ±50%. Assuming the tabulated data[2] on titanium are correct, the pressure determinations on titanium in this study show the relative cross sections $\sigma_{Ti} / \sigma_{Ag}$ to be in error by less than ±50%, and thus the ratio σ_B / σ_{Ti} is known to at least a factor of two. These observations are consistent with those of Searcy, et al[6] for the free surface vaporization of TiB_2. The multiplier response for Ag, B, and Ti was measured in this work with an uncertainty of ±10%. All thermodynamic results taken from tabulated data were assumed to be without error.

V. DISCUSSION

Partial pressures of titanium and boron have been determined over condensed phases of the Ti-B-C system for several regions of the phase diagram. The first set of measurements was made in the region TiB_2-B_4C-B, where boron and TiB_2 powders were used in a B_4C crucible. The second set of measurements was made with TiB_2 powder loaded in a graphite crucible, ostensibly along the line TiB_2-C in the phase diagram. The third set of measurements was made with titanium metal added to the TiB_2 powder in the graphite crucible used for the

second set of measurements. Results for the heat of vaporization and formation of TiB_2 are in excellent agreement, giving an average $\Delta H^o_{298} = 429.8$ kcal/mole and an average $\Delta H^o_{298} = -52.1$ kcal/mole, respectively.

As discussed by Brewer and Haraldsen[1] the observation that $TiB_2(s)$ is stable in graphite bounds the stability of TiB_2 relative to TiC. Using the data of Humphrey[13] for TiC one finds $\Delta H^o_f (TiB_2) \leq -44$ kcal/mole while the data of Fujishiro and Gokcen[14] would yield $\Delta H^o_f (TiB_2) \leq -31.3$ kcal/mole. Brewer and Haraldsen state that the heats of formation of titanium borides should be about -36 kcal/mole of boron. The agreement between this result and that of Samsonov[5] for TiB_2 is apparently fortuitous since Samsonov used a value -66 kcal/mole for the heat of formation of B_4C in disagreement with the value used by Brewer and Haraldsen and with recently tabulated values.[2] The present results for TiB_2 do not agree with $\Delta H^o_f = -72$ kcal/mole.

The measurements of Schissel and Williams[3] yield $\Delta H^o_f \cong -32$ kcal/mole for TiB_2. These mass spectrometric measurements were made with a mixture of boron and TiB_2 powders contained in a TiB_2 crucible which was held in a tungsten outer jacket. The boron pressure determinations are in agreement with the data of this report although the titanium pressure was anomalously high. The discrepancy in the titanium pressure is believed to be due to titanium vapor escaping from the region between the TiB_2 cell and the tungsten jacket, possibly enhanced by reaction with the tungsten, thus leading to erroneous heats of vaporization and formation of TiB_2. In a recent experiment with a high temperature calorimeter Lowell and Williams[7] obtained $\Delta H^o_f = -50\pm5$ kcal/mole for TiB_2 in agreement with the result of the present investigation.

The question of vaporization coefficients has not been systematically investigated but the values of σ for the two cells were different by one decade and resulted in a statistically insignificant difference in the TiB_2 values.

The observation that TiB is found with TiB_2 after samples of the appropriate composition range are heated does not preclude the possibility that TiB is stable over a limited temperature range only. However, for TiB(s) to be unstable at low temperatures relative to Ti(s) and TiB_2 (s), the heat of the reaction Ti(s) + $TiB_2(s) \rightarrow 2\,TiB(s)$ must be positive.[15] The value found in this research is -16 kcal/mole. TiB may be unstable at some temperatures relative to decomposition to TiB_2 plus a titanium rich phase, however. If, as suggested by Hansen and Anderko,[16] TiB decomposes at temperatures above about 233 0 °K by the reaction $3\,TiB(s) \rightarrow Ti_2B(s) + TiB_2(s)$, a few of these measurements may have been made for Ti_2B and TiB_2 mixtures. However, ΔF must be small for the decomposition reaction near the transition point, and no significant error is introduced by the assumption that TiB was the phase present with TiB_2.

ACKNOWLEDGMENT

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TABLE I

CALCULATION OF THE HEAT OF VAPORIZATION AND
HEAT OF FORMATION OF TiB₂(s)

System Before Heating	Run	T (°K)	-log P_B	-log P_{Ti}	-log K	ΔF° (kcal/mole)	ΔH°_{298} (kcal/mole)		$-\Delta H^\circ_f$ (kcal/mole)	
B+TiB₂ in B₄C	1	2244		8.47	18.92	194.3	427.5		49.8	
		2296		8.46	18.33	192.6	430.9		53.2	
		2347		8.26	17.62	189.2	432.6		54.9	
		2357		8.44	17.69	190.8	435.2		57.5	
		2382		7.97	16.98	185.0	432.0		54.2	
		2398		7.96	16.81	184.4	432.9		55.2	
		2408		7.74	16.50	181.8	431.2		53.5	
	2	2306		8.40	18.16	191.7	431.1		53.3	
		2462		7.38	15.64	176.2	431.0		53.3	
	3	2411		7.56	16.29	179.7	429.5		51.8	
								431.4		Avg. 53.7±0.7
TiB₂ in C	4	2192	6.54	7.19	20.27	203.3	431.4		53.7	
		2185	6.62	7.11	20.36	203.5	430.9		53.2	
	5	2353	5.14	6.31	16.60	178.7	422.7		45.0	
	6	2246	6.20	7.12	19.52	200.6	434.1		56.3	
		2246	6.22	7.00	19.44	199.8	433.2		55.5	
		2246	6.13	7.04	19.30	198.4	431.8		54.1	
		2278	5.78	6.83	18.40	191.8	428.3		50.6	
		2278	5.73	6.78	18.23	190.1	426.6		48.9	
		2278	5.77	6.79	18.33	191.1	427.6		49.9	
		2310	5.57	6.83	17.97	189.9	429.7		52.0	
								429.6		Avg. 51.9±1.1
Ti+TiB₂ in C	7	2271	6.22	6.02	18.46	191.8	427.7		50.0	
		2269	6.18	6.21	18.56	192.7	428.4		50.7	
		2269	6.11	6.29	18.51	192.1	427.9		50.1	
		2307	5.93	6.21	18.06	190.6	430.1		52.4	
		2063	7.61	7.92	23.15	218.5	433.7		56.0	
		2107	7.04	7.59	21.68	209.0	428.6		50.9	
		2272	6.01	6.44	18.45	191.8	427.8		50.1	
	8	2276	5.96	6.55	18.47	192.4	428.8		51.0	
	9	2266	6.61	5.35	18.56	192.5	427.9		50.2	
	10	2340	6.11	4.96	17.18	183.9	426.7		49.0	
		2327	6.05	5.37	17.47	186.0	427.5		49.7	
								428.6		Avg. 50.9±0.7

FIGURE 1

**THE CLAUSIUS-CLAPEYRON PLOT FOR B$^+$(g). LOGARITHM OF
THE INTENSITY OF B$^+$(g) TIMES THE ABSOLUTE TEMPERATURE
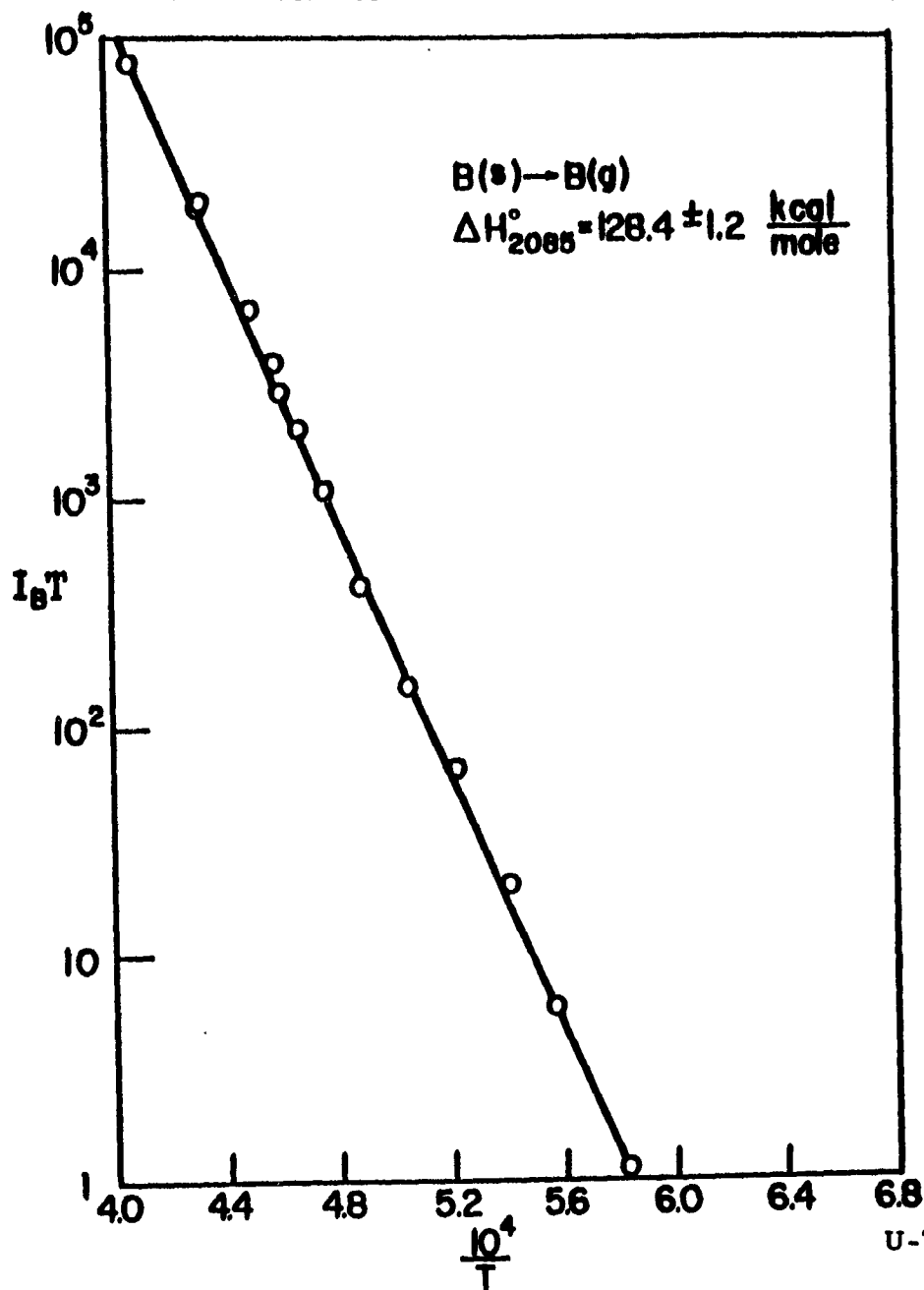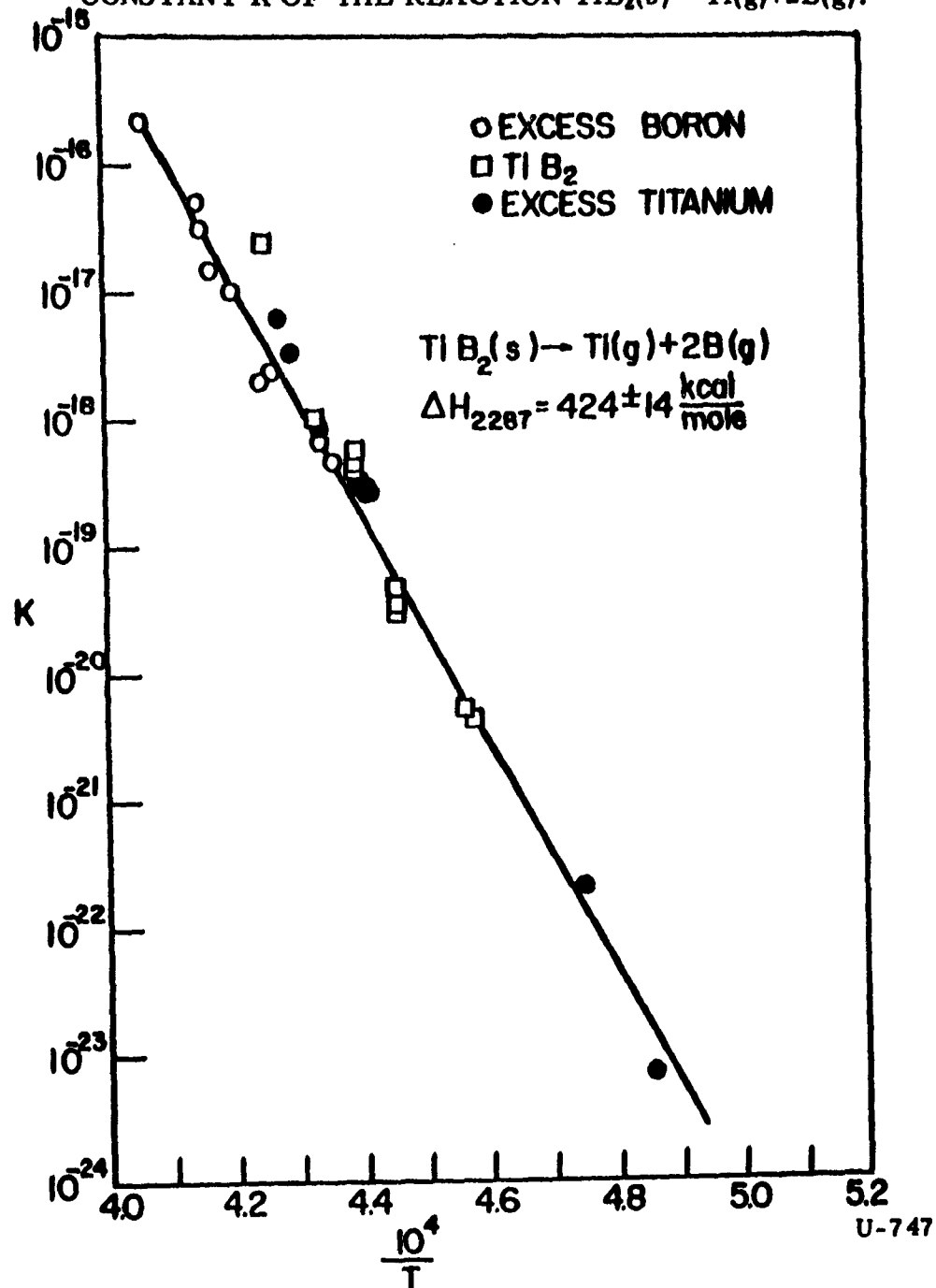VS THE RECIPROCAL ABSOLUTE TEMPERATURE.**

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